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- 1 -

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ZERO VOLATILE ORGANIC COMPOUND COMPOSITIONS BASED UPON ORGANIC SOLVENTS WHICH ARE NEGLIGIBLY REACTIVE WITH HYDROXYL RADICAL AND DO NOT CONTRIBUTE APPRECIABLY TO THE FORMATION OF GROUND BASED OZONE

Cross-Noting to Related Applications

This application claims the benefit of U.S. Provisional Application No. 60/053,073, filed July 18, 1997.

Background of the Invention

5 This invention pertains to the art of solvent blends and solvent/resin blends. More, particularly this invention pertains to blends that do not contribute to the formation of ground based ozone or smog. The invention is particularly applicable to solvent blends and  
10 solvent/resin blends that have no volatile organic compounds for use with adhesives, coatings, inks, cleaning and blowing agents and the like and will be described with particular reference thereto. However, it will be appreciated that the invention may be advantageously  
15 employed in other environments and applications.

Heretofore, hydrocarbon-based solvents have been used to dissolve organic materials in many industrial applications. However, recently, hydrocarbon-based solvents have fallen out of favor because they have been  
20 classified by the United States Environmental Protection Agency and other international regulatory bodies as materials that contribute to the formation of ground based ozone or smog. This has created a need for other types of solvents for the production of coatings, adhesives, inks  
25 and the like.

Upon evaporation, a highly-reactive, hydrocarbon-based solvent reacts with hydroxyl radicals and ultraviolet light very close to the ground to form a photochemical smog that is considered harmful and in some

cases dangerous. Some cities have severe smog which reduces visibility and actually causes "ozone alerts". In part, the smog is caused by hydrocarbon emissions from cars. However, another major contributor is industrial use of hydrocarbon-based solvents such as hexane and toluene.

The benchmark for desired reaction rates of hydrocarbon-based compounds is ethane. If a compound has a reaction rate with the hydroxyl radical and ultraviolet ("UV") light that is faster than ethane, the compound reacts too close to the ground and consequently generates ozone and smog. Such compounds are defined as volatile organic compounds (VOCs). On the other hand, if a compound has a reaction rate that is slower than ethane, the compound reaches higher into the atmosphere before reacting with the hydroxyl radical and UV light. In such instances the non-VOC compound does not contribute to the formation of ground based ozone and smog.

Some of the more reactive VOCs are:

toluene;  
methyl ethyl ketone;  
diacetone alcohol;  
hexane;  
isopropyl alcohol;  
pentane;  
dibasic esters;  
trichloroethylene;  
benzene;  
ethyl acetate;  
butyl acetate;  
n-methyl pyrrolidone;  
glycol ethers;  
d-limonene;  
terpene hydrocarbon solvents;  
dimethyl ether; and,  
tetrahydrofuran.

Governmental regulations limit the use of VOCs in coatings, inks, and adhesives. As a result, water-borne coatings have become the most important type of coatings in coating and adhesive systems. However, water-borne coatings must contain some volatile organic compound content. This is because water flashes off too fast from the water-based latex or emulsion to make a good film. To alleviate this problem, 7-10% of a slower evaporating solvent such as a glycol ether is added to the latex to aid in film formation. Unfortunately, glycol ethers are primary examples of VOCs and thus dangerous to the environment.

Halogenated hydrocarbon-based compounds have reaction rates that are slower than ethane. However, these halogenated compounds are ozone depleting. consequently, they are not suitable VOC-free solvents.

In the prior art, United States Patent No. 5,102,563 to Desbiendras describes a solvent composition which contains methyl tert butyl ether. However, methyl tert butyl ether is a VOC and thus unsafe for the environment. Similarly, Patent No. 4,898,893 to Ashida describes a composition for making a blowing agent which contains a flammable aliphatic hydrocarbon. This is also a VOC. Patent No. 3,950,185 to Toyama teaches film removing compositions which contain methylene chloride and bromochloromethane which are not VOCs. However, these compositions also contain methanol and monochlorobenzene which are VOCs. Patent No. 3,924, 455 to Begishagen describes a formulation containing mineral spirits which removes lacquer stress coatings. These mineral spirits are also VOCs.

An object of the present invention is the identification of some high-performance solvents and solvent/resin blends which are non-flammable or self-extinguishing and do not contribute to the formation of ground-based ozone.

Another object of the present invention are solvents and solvent/resin blends that are safer to the environment than even water-based systems which still must contain a volatile organic solvent to aid in film formation.

Yet another object of the present invention are environmentally-safer solvent compositions which do not contribute to the formation of ground based ozone which will be useful in the formulation of cleaning agents, coatings, adhesives, inks and also blowing agents for the production of plastic foams.

#### Summary of the Invention

The present invention contemplates new and improved solvent and solvent-resin compositions which overcome all of the above referenced problems and others and which are economical and effective for their intended uses.

In accordance with the present invention, there is provided a solvent-resin composition having generally zero volatile organic compounds (VOCs). The composition consists essentially of a resin component and a solvent component. The solvent component is 5-95% by total volume of the solvent-resin composition and is one or more of the zero-VOC solvents selected from the group consisting of:

chlorobromomethane;  
1-bromopropane;  
n-alkane (C12-C18);  
t-butyl acetate;  
perchloroethylene;  
benzotrifluoride;  
parachlorobenzotrifluoride;  
acetone;  
1,2-dichloro-1,1,2-trifluoroethane;  
dimethoxymethane;

2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane;

1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane; and,  
2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane.

In accordance with a more limited aspect of the invention, the solvent component is present in the amount 40-95% by total volume of the composition.

In accordance with a still more limited aspect of the invention, the solvent component is present in the amount 30%-80% by total volume of the composition.

A principal advantage of the invention is that it is environmentally safer yet still capable of effectively dissolving resins.

Another advantage of the invention is that it may be used in place of solvents currently used for inks, adhesives, coatings and the like.

Still other advantages and benefits of the invention will become apparent to those skilled in the art upon a reading and understanding of the following detailed description.

## Detailed Description of the Preferred Embodiments

The compositions of the present invention are high-performance solvent and solvent-resin blends that are generally free of VOCs. The compositions as herein described and as set forth in the claims are expressed in terms of percentages by volume unless clearly indicated to the contrary.

In describing the compositions of the present invention, reference will be made to certain resin classifications which require a totally VOC-free solvent system to be environmentally safe. These resin classifications are:

- 5 a) acrylic-thermoplastic;  
b) acrylic-thermosetting;  
c) chlorinated rubber;  
d) epoxy (either one or two part);  
e) hydrocarbon (e.g., olefins, terpene  
resins, rosin esters, coumarone-  
indene, styrene-butadiene, styrene,  
methyl-styrene, vinyl-toluene,  
10 nitrocellulose, polychloroprene,  
polyamide, polyvinyl chloride and  
isobutylene);  
f) phenolic;  
g) polyester and alkyd;  
h) polyurethane;  
15 i) silicone;  
j) urea; and,  
k) vinyl and vinyl acetate.

20 It is to be appreciated that this list does not include  
all resin classifications. Other resin classifications  
are intended to be encompassed by the scope of the present  
invention.

Effective solvents of the present invention  
which have reaction rates with hydroxyl ion slower than  
ethane are:

- 25 1) chlorobromomethane;  
2) 1-bromopropane;  
3) methyl acetate;  
4) n-alkane (C12-C18);  
5) t-butyl acetate;  
30 6) perchloroethylene;  
7) benzotrifluoride;  
8) parachlorobenzotrifluoride,  
9) acetone;  
10) 1,2-dichloro-1,1,2-trifluoroethane  
35 11) dimethoxymethane;

- 12) 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane;
- 13) 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane;
- 14) 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane;
- 15) 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane;
- 16) methylene chloride; and,
- 17) technical white oils (mineral oils).

It is to be appreciated that this list does not include all effective non-VOC solvents. Other effective non-VOC solvents are intended to be encompassed by the scope of the present invention.

The type of specific applications (hence the denotation "a" alongside the number identifying the application) for which the solvents and solvent-resin blends of the present invention may be used are as follows:

- 1a) adhesives
- 2a) blowing agents
- 3a) coatings
- 4a) cleaning compositions
- 5a) inks

The zero-VOC solvent and solvent-resin blends of the present invention as well as their applications are set forth in the table below. The table uses the identifiers set out above, i.e., a numeral alone for the solvent and a numeral followed by "a" for the application.

SOLVENT AND SOLVENT-RESIN COMPOSITIONS HAVING ZERO VOCs

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T90X

<u>MAIN COMPONENT</u>	<u>HOW USED</u> (blends are 5-95% or, more preferably, 40-95% by vol.)	<u>RESINS THAT FORM A FILM AFTER SOLVENT EVAPORATES</u>	<u>APPLICATIONS</u>
chlorobromomethane	by itself or blended with any of solvents 2-16 to obtain desired properties	a-k	1a-5a
1-bromopropane	by itself or blended with solvents 1, 3-16	a-k	1a, 3a, 5a
methyl acetate	blended with solvents 1,2, 4-16 at 10-95% by volume.	a-d, styrene, g, j, k	1a-5a
n-alkane (C12-C18)	by itself or blended with solvents 1-3,5-16	e	1a, 3a, 4a, 5a
t-butyl acetate	by itself or blended with solvents 1,4,6-16	a-d, styrene, g, j, k	1a, 3a, 4a, 5a
perchloroethylene	1-5,7-16	a-k	1a,3a,4a,5a
benzotrifluoride	1-6, 8-16	a-k	1a,3a,4a,5a
parachlorobenzotri fluoride	1-7, 9-16	a-k	1a,3a,4a,5a
acetone	1-5,7-16	a, b, e-h, k	1a-5a

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	1,2-dichloro- 1,1,2- trifluoroethane	1-9, 11-16	a, k	1a-5a
	dimethoxymethane	1-3,7-10, 12-16	a	1a-5a
5	1,1,1,2,2,3,3,4,4- nonafluoro-4- methoxy-butane	1-11, 13,15	a	2a, 4a
10	2- (difluoromethoxyme thyl) - 1,1,1,2,3,3,3- heptafluoropropane	1-12, 14,15	a	2a, 4a
15	1-ethoxy- 1,1,2,2,3,3,4,4,4- nonafluorobutane	1-13, 15	a	2a,4a
20	2- (ethoxydifluoromet hyl) - 1,1,1,2,3,3,3- heptafluoropropane	1-4	a	2a,4a
	methylene chloride	2-15	a-k	1a-5a
	technical white oils (mineral)	1-16	a,e,g	5a

A better understanding of the present invention can be had by reference to the following descriptions of embodiments which effectively meet the objectives outlined above.

One preferred embodiment includes mixing one or more of the polymeric resins:

- acrylic-thermoplastic;
- acrylic-thermosetting;
- chlorinated rubber;
- epoxy resin;

hydrocarbon (e.g., olefins, terpene resins,  
rosin esters, coumarone-indene, styrene-  
butadiene, styrene, methyl-styrene, vinyl-  
toluene, nitrocelullose, polychloroprene,  
5 polyamide, polyvinyl chloride and  
isobutylene);  
phenolic;  
polyester and/or alkyd;  
polyurethane;  
10 silicone;  
urea; and/or  
vinyl or vinyl acetate,  
with 10-90%, by total volume of the composition, of one or  
more of non-VOC solvents such as:  
15 chlorobromomethane;  
1-bromopropane;  
methyl acetate;  
n-alkane (C12-C18);  
t-butyl acetate;  
20 perchloroethylene;  
benzotrifluoride;  
parachlorobenzotrifluoride;  
acetone;  
1,2-dichloro-1,1,2-trifluoroethane;  
25 dimethoxymethane; and/or  
methylene chloride.

The individual solvents or blends thereof are added until  
all of the resin(s) is dissolved.

In an embodiment for coatings and/or adhesives,  
30 the mixture preferably has a high resin content, i.e., a  
resin content of 20%-60% by volume. In another embodiment  
for inks, the mixture preferably contains a lower  
concentration of the resin, i.e., 5%-30% by volume. In  
yet another embodiment, various pigments or additives are  
35 added to achieve a desired range of properties.

In another preferred embodiment of the present  
invention, 5-90% methyl acetate, by total volume of the

composition, is added to 10-95% of a solvent or solvent blend selected from the group:

chlorobromomethane;  
1-bromopropane;  
5 n-alkane (C12-C18);  
t-butyl Acetate;  
perchloroethylene;  
benzotrifluoride;  
parachlorobenzotrifluoride;  
10 acetone;  
1,2-dichloro-1,1,2-trifluoroethane;  
dimethoxymethane;  
1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-  
butane;  
15 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane;  
1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane; and,  
2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane.  
20

These formulations are used as a cleaning composition for the removal of hydrocarbon or ionic contaminants from circuit boards or in the formulation of coatings, inks, or adhesives. Of course, the formulations may be used for  
25 other applications as well.

The following enumerated embodiments have the ability to dissolve resins for the production of coatings, adhesives, and inks as well. In addition, the embodiments are equally useful as cleaning formulations. The ranges  
30 for the embodiments are expressed in % by volume of the total solvent-resin composition or, alternatively, the total solvent composition of an initially non-resin containing solvent, such as a cleaning composition. The embodiments are:

- 35 (1) 10-90% benzotrifluoride and 10-90% of one or more of the solvents:

- 5 (a) 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane;  
(b) 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane;  
(c) 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane;  
(d) 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane;  
10 (e) perchloroethylene;  
(f) 1-bromopropane;  
(g) acetone;  
(h) n-alkane (C12-C16);  
(i) t-butyl acetate (C12-C16); and,  
(j) parachlorobenzotrifluoride;  
15 (2) 5-20% benzotrifluoride and 80-95% 1-bromopropane;  
(3) 10-90% acetone and 10-90% n-alkane (C12-C18);  
(4) 10-90% 1-bromopropane and 10-90% of one or more  
of:  
20 (a) chlorobromomethane; and,  
(b) n-alkane (C12-C18);  
(5) 10-90% parachlorobenzotrifluoride and 10-90% of  
one or more of:  
25 (a) 1-bromopropane;  
(b) chlorobromomethane;  
(c) t-butyl acetate; and,  
(d) n-alkane (C12-C18);  
(6) 10-90% 1,2-dichloro-1,1,1-trifluoroethane and  
10-90% of one or more of:  
30 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane;  
2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane;  
1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane;  
and,  
35 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane;  
1-bromopropane

acetone;  
benzotrifluoride; and,  
methyl acetate.

5 Analogously, the following VOC-free embodiment has the ability to dissolve resins for the production of coatings, adhesives, and inks as well. In addition, the embodiment is equally useful in cleaning formulations:

10-90% methylene chloride and 10-90% of one or more of the following solvents:

10 chlorobromomethane;  
1-bromopropane;  
methyl acetate;  
n-alkane (C12-C18);  
t-butyl acetate;  
15 perchloroethylene;  
benzotrifluoride;  
parachlorobenzotrifluoride;  
acetone;  
1,2-dichloro-1,1,2-trifluoroethane; and,  
20 dimethoxymethane.

An added benefit to mixing methylene chloride with other solvents is the reduction in the overall toxicity of methylene chloride.

25 Other preferred solvent-resin compositions include VOC-free solvents which have the ability to dissolve resins for the production of coatings, adhesives, and inks. The compositions include any of the above-listed resins and the following solvent mixtures, which are expressed in terms of % by volume of the solvent-resin composition:

- 30 (1) 1-20% technical white oil and 10-90% n-alkane (C12-C18);  
(2) 1-20% technical white oil and 10-90% methyl acetate;  
35 (3) 1-20% technical white oil and 10-90% t-butyl acetate;

(4) 1-20% technical white oil and 10-90% benzotrifluoride;

(5) 1-20% technical white oil and 10-90% acetone;

5 (6) 1-20% technical white oil and 10-90% parachlorobenzotrifluoride;

(7) 1-20% technical white oil and 10-90% parachlorobenzotrifluoride;

(8) 1-20% technical white oil and 10-90% perchloroethylene;

10 (9) 1-20% technical white oil and 10-90% methylene chloride; and,

(10) 1-20% technical white oil and 10-90% of a mixture of methylene chloride, acetone, t-butyl acetate, methyl acetate and perchloroethylene.

15 The following VOC-free embodiment, expressed in terms of % by volume of total composition, is useful as an environmentally-safer blowing agent composition for the production of polyurethane or isocyanurate foams:

20 99-99.98% 1,2-dichloro-1,1,1-trifluoroethane and 0.01-0.5% alpha-methyl styrene to inhibit polymerization. In addition this embodiment has the ability to dissolve resins for the production of coatings, adhesives, and inks, and is useful in cleaning formulations.

25 Another embodiment useful as an environmentally-safer blowing agent composition is:

100 parts by weight polyether triol;

50 parts by weight toluene diisocyanate or toluene diisocyanurate;

30 2 parts by weight water;

0.15 parts catalyst;

0.5-2 parts surfactant; and,

4-10 parts 1-bromopropane or chlorobromomethane.

35 Still another embodiment useful as an environmentally-safer blowing agent composition, in terms of percent by weight of the total composition (including catalyst and surfactant), is:

50-70% polyether triol;  
20-40% toluene diisocyanate or toluene  
disocyanurate;

0-10% water;

5 0-5% catalyst;

0-5% surfactant;

2-15% 1-bromopropane or chlorobromomethane. The  
appropriate catalysts and surfactants are selected from  
those known in the art.

10 A more limited embodiment useful as an  
environmentally-safer blowing agent composition, in terms  
of percent by weight of the total composition (including  
catalyst and surfactant), is:

60-65% polyether triol;

15 30-33% toluene diisocyanate or toluene  
disocyanurate;

1-2% water;

0.09-2% catalyst;

0.3-1.5% surfactant; and,

20 2.4-6.1% 1-bromopropane or chlorobromomethane.

This composition is useful for the manufacture of a  
flexible furniture grade foam with a density of 0.024  
g/cm<sup>3</sup>. blowing agent.

25 An embodiment of a zero-VOC adhesive is 350  
grams of 1-bromopropane and/or benzotriflouride to which  
is added 30-50% by weight of a hydrocarbon resin,  
preferably an olefin, rosin ester or terpene resin, which  
acts as a tackifier. Then, 100 grams of styrene-butadiene  
polymer, polychloroprene polymer, polyvinyl chloride  
30 polymer, acrylic, epoxy, urethane, nitrocellulose, or  
styrene is added to the mixture. This mixture produces a  
contact adhesive with excellent bond strength. Another  
preferred embodiment of this mixture contains  
approximately 40-90%, volume, of 1-bromopropane and/or  
35 benzotriflouride, 5-35% of a hydrocarbon resin, and 5-25%  
of styrene-butadiene polymer, polychloroprene polymer,

polyvinyl chloride polymer, acrylic, epoxy, urethane, nitrocellulose, or styrene.

Another zero-VOC adhesive starts with 100 grams of 1-bromopropane and/or benzotrifluoride. Then, 10-100 grams of styrene-butadiene, polychloroprene, polyvinyl chloride, acrylic, epoxy, urethane, nitrocellulose, or styrene polymer or resin is added. This also produces a contact adhesive with excellent bond strength. It is appreciated that other additives may be used to improve wetting and defoaming although they are not always required. Another preferred embodiment of this mixture contains approximately 40-95%, by volume, of 1-bromopropane and/or benzotrifluoride, and 5-60% of styrene-butadiene, polychloroprene, polyvinyl chloride, acrylic, epoxy, urethane, nitrocellulose, or styrene polymer or resin. Still another preferred embodiment of this mixture contains approximately 70-95%, by volume, of 1-bromopropane and/or benzotrifluoride, and 5-30% of styrene-butadiene, polychloroprene, polyvinyl chloride, acrylic, epoxy, urethane, nitrocellulose, or styrene polymer or resin.

Still another embodiment of a zero-VOC adhesive starts with 350g 1-bromopropane and/or benzotrifluoride. Then, 20-100 grams of styrene butadiene rubber is added. Optionally, 5-10%, by volume, acetone is added to improve solubility if necessary. Another preferred embodiment of this mixture contains approximately 50-90%, by volume, of 1-bromopropane, and 10-30% of acrylic polymer or urethane polymer. Optionally, 5-10%, by volume, acetone is added to improve solubility if necessary.

The following VOC-free embodiment has the ability to dissolve resins for the production of coatings, adhesives, and inks as well. Further, the solvent includes stabilizers to stabilize against attack on aluminum. In addition, the embodiment is useful in cleaning formulations:



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